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A new method for ash melthod thermo-analysis based on mineral quantity

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Ash deposition has a major impact on safe and economic operation of coal-fired boiler. A new method for ash melting thermo-analysis based on X-ray diffraction mineral quantitative analysis was developed; the classical thermal analysis theory was used to describe the dynamic behavior of ash melting. The low-temperature ash melting process curve was acquired. Compared with the conventional method of ash fusibility, the new method of ash melting characteristic curve reflects the ash melting dynamic better. The ash melting characteristic curve reveals the multi-stage reaction process of minerals melting, explains the gradual increase of mineral melting process in theory.

mineral quantitative thermo-analysis, melting, ash deposit

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The melting behavior of ash particles and viscosity of deposit are two decisive factors of slagging [1]. Recently, many studied reported the ash deposition, a variety of methods have been widely used to speculate ash melting behavior [1–6]. The most commonly used is the ash fusion temperature method based on the image recognition. However, the reproducibility of this method is poor and the sample preparation process of this method is complicated. In addition, even more noteworthy is that only four instantaneous characteristic temperatures can be given by this method, and the transformation process of minerals and real-time behavior of ash particles in the actual boiler can not be predicted [2,3]. Another defect of this method is that the ash fusion temperatures are just reflecting the melting behavior of ash particles, which is essentially different from the melting behavior of minerals in a boiler. Some studies have shown that the melting temperature of deposit in a boiler is less than that of ash prepared in a lab-scale reactor [5]. Therefore the study on the melting characteristics of minerals in coal must integrate their migration and transformation behaviors during coal combustion.

In addition, a multi phases diagram has been used to analyze the melting of coal ash broadly [2,7,8]. Phase diagram can explain the co-fusion of multi-components very well. However, this method is based on the chemical composition of elements, not taking into account the mineral structure in ash. While for ashes which have the same chemical composition, the varied crystal structure may lead to significant difference in the melting characteristics of ash.

According to the current research status and existing problems, this paper proposes a new method for ash melting thermo-analysis based on mineral quantitative analysis (MQTA). The Rietveld mineral quantitative analysis method and simultaneous thermal analysis (STA) method are combined. The temperature change thermal curve, mineral structure evolution and weight loss data are obtained simultaneously. The STA thermal curve is transformed to ash melting curve in real-time, which has great significance on the study of dynamic process of mineral partition and melting.

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1 Theoretical basis of mineral melting thermo-analysis

The reaction rate of gas solid chemical reaction can be acquired easily to apply thermal gravimetric analysis. Compared with ordinary gas solid reaction, melting process has significant difference. Melting reaction is a complex physical-chemical process that the reactant mass changed little. The slight mass change is not enough to characterize the reaction progress accurately. Therefore, a simple TGA experimental method cannot be used for melting mechanism studies. The thermal analysis is more suitable for the investigation of reaction dynamic.

The progress of melting reaction is proportional to the endotherm during the process, thus the reaction progress can be reflected by DSC curve. The reaction kinetic can be established based on DSC signal which reflects melting energy in theory. As shown in Figure 1, S is the area between DSC curve and baseline of the whole reaction process, S' is the area of a certain time during the reaction process. The DSC signals represent heat flow $\mathrm{d}H/\mathrm{d}\tau$, then S can be used to represents the reaction heat. The reaction fraction of a certain time can be expressed as follows:

$$a = \frac{H}{H_0} = \frac{S'}{S}, \tag{1}$$

where α is reactant conversion rate, H is heat of the reaction for the moment, H_0 is total heat of the reaction.

At this point the concentration of reactant can be calculated as follows:

$$1 - a = \frac{H_0 - H}{H_0} = \frac{S - S'}{S} = \frac{S''}{S}. \tag{2}$$

The STA method based on TGA-DSC has been used to characterize the melting reaction of a single component successfully [4,5]. In order to know the reaction heat, the temperature which obtained simultaneously with TGA can be used to compare with inert reference. The melting reaction is an endothermic process without weight change. The DSC signal of pure compound melting showed a single endothermic peak. So if we know the melting enthalpy, the DSC curve can be transformed into melting curve easily. However, for the ash with complex composition, different components melt at different temperatures that will result in the overlap of endothermic peaks. In addition, the formation process of ash not only contained ash melting but also accompanied the evaporation of some components. Thus in order to obtain the melting curve from STA curve, the heat related to other processes than melting must be subtracted from the raw DSC signal first.

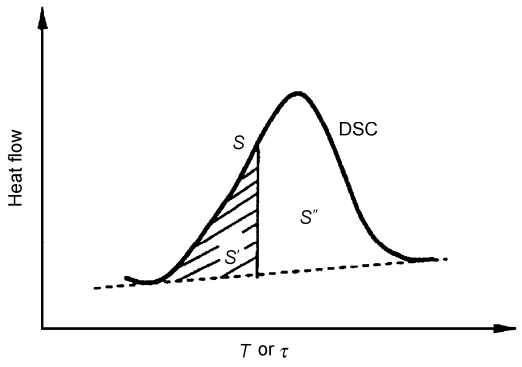

Figure 1 Melting reaction DSC curve.

Mineral evaporation is the source of ash deposits in coal-fired boiler. The initial deposit derived from the condensation of inorganic vapors made melted particles adhere on the heat transfer surface easier [6,9,10]. Thus, a precise quantitative description of the mineral evaporation is of great significance to reveal the mechanism of ash deposition and to mitigate slagging on the heat transfer surfaces of the boiler. The STA method used by Hansen et al. was just to characterize the melting of ash which belongs to the second reaction [4]. It does not accurately reflect the melting of minerals during coal combustion. The proposed MQTA method in this paper is to first use low-temperature plasma ashing method to separate the inorganic minerals from coal, and then conduct the STA analysis of low temperature ash (LTA) to get the TGA-DTA-DSC curves. At last, Rietvild mineral quantitative method is combined to subtract the energies of mineral transformation and evaporation processes.

2 Mineral thermo-analysis curves

Three typical coals (XLT, SF, YZH) were selected to carry out MQTA analysis, and the melting characteristics of coals with different mineral composition were discussed. Thermo gravimetric analysis was conducted on STA 409 thermal analyzer made by German NETZSCH company. The computer-controlled system for temperature-programmed was used in this analyzer, and the weight loss with temperature change was recorded by microbalance system. Experiment temperature range is between 30°C and 1450°C, the heating rate is 50°C/min, the flow rate of air is 100 mL/min. Each sample is about 5 mg.

The typical STA curves of XLT-LTA are shown in Figure 2. There are five obvious weight loss peaks in the DTG curve, locating at 120°C, 380°C, 590°C, 740°C, and 1200°C, respectively. Combining the mineral quantitative result (Table 1), it is easy to find that the weight loss peak at 120°C and 380°C belong to the dehydration of adsorbed water and hydrated gypsum mineral. The peak at about 590°C represents the decomposition of kaolinite and illite, 740°C peak originates from the weight loss of calcite decomposition.

Table 1 Mineral composition and content in XLT-LTA (wt%)

Coal sample	XLT	Coal sample	XLT
LTA	18.7	Calcite	13.8
Kaolinite	8.5	Bassanite	23.6
Illite	21.3	Pyrite	5.5
Quartz	22.9	Anatase	4.4

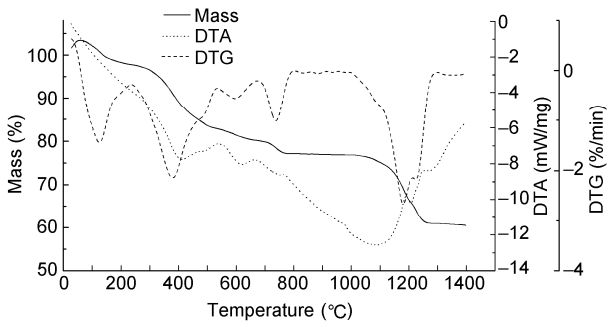

Figure 2 TG-DTA-DTG curves of XLT-LTA in air.

The peak at about 1200°C is the overlap of two weight loss peaks.

The mineral composition of XLT-LTA (Table 1) indicated that there is no decomposition weight loss reaction after the temperature rising to 1000°C. Whereas, two endothermic peaks were found from the DSC curve around 1200°C. This result implies that the weight loss peaks at about 1200°C were mainly due to the mineral evaporation. The further detailed analysis shows that, there is a weak endothermic peak without weight loss from point A (809°C) to point B (1013°C) in the DSC curve (Figure 3). This is a typical melting process. As the temperature increased further, sample weight begins to decrease rapidly until the point C (1277°C), after that the weight of sample keeps constant. There are obvious endothermic peaks between BC and CD in DSC curve, the BC section with an obvious weight loss has mineral composition evaporation, whereas the CD section without mass change belongs to another melting process.

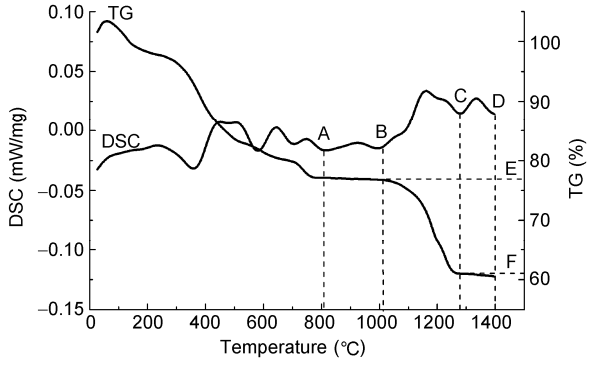

Figure 3 TG-DSC curves of XLT-LTA-air.

The integral calculation of total heat was conducted, starting from point A to point D, the area under the blank baseline was subtracted to get the total thermal change of mineral melting and evaporation (Figure 4). The evaporation process is usually accompanied by mineral melting, so the thermal effect of segment BC is not entirely mineral evaporation, but rather a combination of mineral melting and evaporation. To accurately quantify the mineral melting process, the mixed thermal effects of segment BC should be distinguished. However, due to the complex mineral composition in LTA, the direct calculation of thermal effect of melting process is very difficult. Each component melts at different temperatures, and sometimes different components may be co-fusion. In comparison, the evaporation enthalpy of mineral composition is relatively easy to calculate. The evaporation process is mainly focused on the 1013°C to 1277°C for this coal, and the total weight loss of evaporation can be acquired easily from TG curve (segment EF). So here we use an approximate method to estimate the enthalpy of vaporization, and then use the total heat minus the heat of evaporation to get the melting endotherm, thus the relationship between melting heat change and temperature can be constructed.

The mineral composition of XLT-LTA includes kaolinite, illite, quartz calcite, and bassanite. The contents of minerals are listed in Table 1. The vaporization enthalpy of each component can be obtained from thermodynamic database. So the concept of average evaporation enthalpy of LTA H_{LTA} is defined as follows:

$$H_{\mathrm{LTA}} = \sum_{1}^{n} H_i C_i, \tag{3}$$

where H_i is the evaporation enthalpy of component i, C_i is the content of component i.

The average evaporation enthalpy of XLT-LTA was calculated, as about 10.57 kJ/g. Assume that the average evaporation enthalpy is not changed after component melting, so the evaporation enthalpy during BC section can be calculated by the total weight loss. The mass change can be

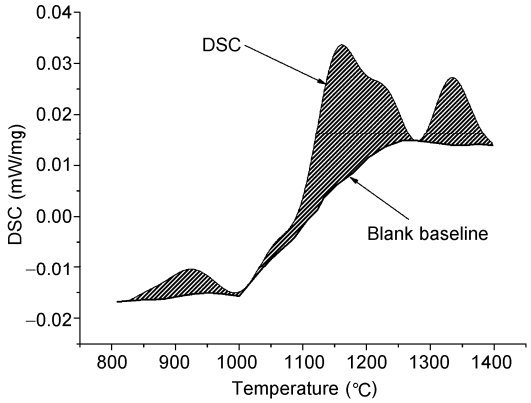

Figure 4 Mineral melt heat curve.

read from TG curve is about 15.7% (segment EF), the total mass of ash sample is known, so the evaporation enthalpy of BC segment can be calculated, is about 8.29745 J. Assuming the evaporation is proportional to temperature, and then the mixed thermal effect in Figure 4 can be separated, the single melting heat curve can be calculated (Figure 5). The shape of melting curves with and without subtract evaporation enthalpy are similar. The mineral melting of XLT coal is a typical multi-stage process, these two melting curves reflected the melting process accurately. However, the melting rate at high temperature is faster than that at low temperature, so the melting curve subtracted the evaporation enthalpy is more reasonable.

Compared with the ash fusion temperatures that determined by national standard GB/T219-1996 (Figure 6), the temperature of mineral began to melt is 300°C, lower than the initial deformation temperature (IDT), which is consistent with the results of Hansen [4, 5]. Huggins and Huffman also found that the temperature of ash began to melt is 200–400°C, lower than IDT [5]. The ash melting temperature in STA experiment measured by Hansen is about 150°C lower than IDT. For XLT-LTA, when the temperature reached at IDT, the XLT-LTA already has 12% of the mineral melted (Figure 6). In Hansen's experiments, the biomass ash already has 51% components melted, coal ash has up to 36% components melted [4]. However, the mineral melt has not increased significantly with the temperature rising from hemispherical temperature (HT) to flux temperature (FT).

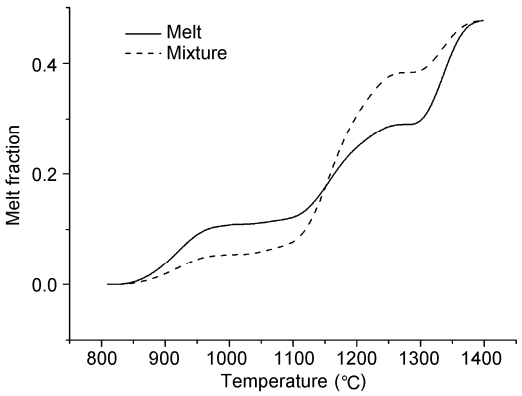

Figure 5 Melting curve of minerals.

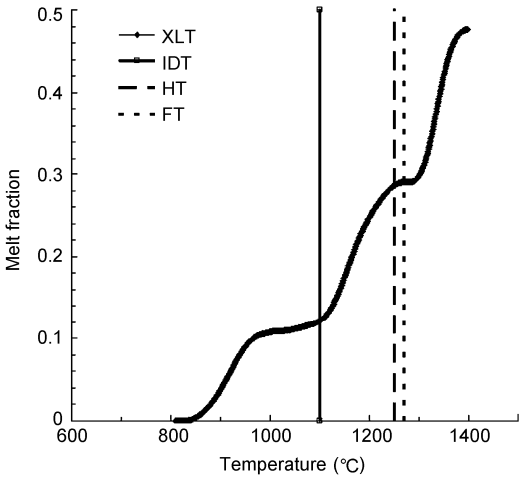

Figure 6 Comparison of melting curve and ash fusion temperatures of XLT.

The ash fusion temperature is related to its chemical composition and the ratio of acidic oxides and alkaline oxides. Normally, ash is difficult to melt with the increase of acidic oxides like Al_2O_3 content. Whereas, the alkaline oxides like Fe_2O_3, CaO, K_2O, etc. can promote the ash fusion. However, due to the complexity of coal composition, the same chemical composition of coal sample, in the mineral composition can vary widely. Most of the previous studies focused on differences in chemical composition of ash, but ignored the impact of original mineral composition of coal. Based on the above-mentioned MQTA method, three typical easy-slagging coal samples (XLT, SF, YZH) were selected to conduct the experimental analysis. The melting curves of these three LTAs are shown in Figure 7. The initial melting temperature of XLT-LTA is the lowest, and the melting percent at 1400°C is also the lowest, only 47.7%. The YZH-LTA has the largest melting percent, up to 79.9% at 1400°C. Although both of them have similar chemical compositions, the melting characteristics are different. This also validates that the mineral composition has significant influence on ash fusion. Similar to XLT-LTA, the melting processes of SF-LTA and YZH-LTA have obvious multiple stages. The initial stage is slow, and then the reaction rate increase sharply. This is mainly because of the various mineral compositions of LTA samples. The mixture eutectic happened during the melting process which accelerated the fusion of minerals [1].

3 Conclusions

The ash melting behavior plays an important role in the

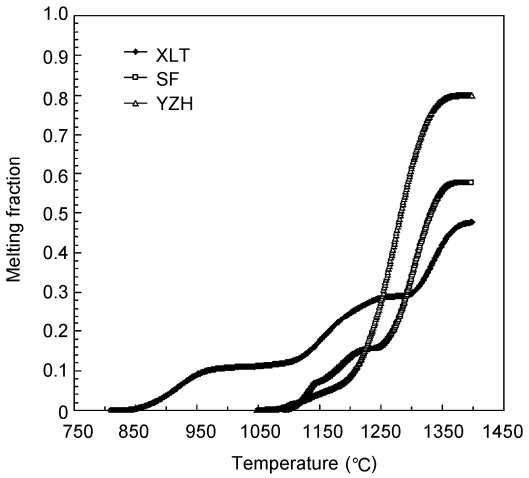

Figure 7 Melting curves of different coal samples.

evaluation of coal slagging. In this paper, a new method based on mineral quantitative analysis and melting thermoanalysis (MQTA) was established to characterize the melting process. The ash melting curves were calculated. Compared with the normal ash fusion temperature, the ash melting curve can reflect the variation of ash fusion process better. The melting of minerals in coal is a multi-stage reaction process. As the reaction took place, the melt reaction rate gradually increased, and then the reaction rate tended to moderate. The melting curve that provides the dynamic melting process has great significance on the slagging prediction of coal-fired utility boiler.

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